OXIDATION OF SO_2 INTO RECOVERABLE AQ.H_2SO_4 OVER PITCH BASED ACTIVE CARBON FIBERS

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INTRODUCTION

The present authors have proposed a novel base for the removal of SO_2 in the flue gas where SO_2 is adsorbed, oxidized and hydrated over PAN-ACF to be continuously recovered in the form of aq. H_2SO_4.[1-3] Higher activity of ACF and less amount of humidity are wanted for smaller volume of the reactor, recovery of more concentrated H_2SO_4 and less consumption of water to reduce the cost of flue gas cleaning.

The present authors have found significant enhancement of the catalytic activity of PAN-ACF by the heat-treatment at 800°C.[4.5]

In the present study, catalytic activities of pitch based ACFs of high surface area were examined for the oxidative removal of SO_2. Pitch based ACF of as-received form has been reported to be inferior to PAN-ACF in the oxidative adsorption of SO_2.[5] However the heat-treatment is expected to enhance its catalytic activity. Hence the heat-treatment at rather high temperatures above 1000°C was examined to find higher activity. The hydrophobic surface of pitch based ACF can be expected to require smaller amount of H_2O for the complete removal of SO_2.

EXPERIMENTAL

OG series of pitch based ACF were supplied by Osaka gas Co.. It was heat-treated in nitrogen gas at several temperatures. Some of their properties are summarized in Table 1. SO_2 removal was carried out at 30°C, using a fixed bed flow reactor. Weights of ACF were 0.1 and 0.25g. The total flow rate was 100ml/min. The model flue gas containing SO_2 of 500-1000ppm, O_2 of 5vol% and H_2O of 5-20vol% in nitrogen was used. Aq.H_2SO_4 was recovered at the outlet of the reactor. SO_2 concentrations in the inlet and the outlet gases were observed continuously by a flame photometric detector (FPD) and NOx gases were analyzed by NOx meter (ECL-88US, Yanagimoto Co.,Ltd.).

Temperature programmed decomposition (TPDE) spectra of the ACFs were measured by using a quartz-glass apparatus equipped with a mass spectrometer (AQA-200, ANELVA INC.) The sample of 0.1g was heated in helium flow up to 1100°C with 10°C/min increments and the evolved gases such as COand CO_2 were analyzed by the mass spectrometer.

RESULTS

The effects of heat-treatment temperature

Figure 1 illustrates the effects of heat-treatment temperature for SO_2 removal over pitch based ACFs. Stationary removal of SO_2 over all fibers was enhanced very much by the heat-treatment above 800°C. The activity was enhanced at higher temperature up to 1100°C. Complete removal was achieved for at least 15h with ACFs heat-treated above 900°C on OG-20A of the largest surface area. The ACF heat-treated at 1100°C removed completely SO_2 at W/F of 1×10^{-3} g min ml^{-1}. The Activity enhancement is remarkable. The large surface area provided the large activity after the heat-treatment among the ACF.

The activity of pitch based ACF OG-20A of the largest surfase area

Figure 2 illustrates the desulfurization profiles of 1000ppm SO_2 by as-received and heat-treated OG-20A at W/F (Weight/Flow) = 1×10^{-3} g·min ·ml^{-1}, 10% humidity and 30°C. The favorable influences of the heat-treatment at higher temperature up to 1100°C were definite. The heat-treatment at 900°C and 1000°C increased the removal up to 40 and 80%, respectively. A further higher temperature of 1100°C removed completely SO_2 of 1000ppm for at least 15h. High temperature of 1200°C decreased the activity to 40% removal. There is certainly an optimum temperature of the heat-treatment with this particular OG-20A of very large surface area.

The effects of H_2O

Figure 3 illustrates the effects of H_2O in the SO_2 removal over OG-20A-H1100 by W/F of 1×10^{-3} g·min ·ml^{-1} at 30°C. Lower concentration of H_2O decreased the extent of SO_2 removal , providing 100% removal at 10% H_2O, 96% at 7.5% H_2O, and 55% at 5% H_2O. Larger W/F of 5×10^{-3} g·min ·ml^{-1} allowed complete removal with 5% H_2O.

The influence of NO

Figure 4 illustrates the influence of NO of 500ppm at SO_2 of 500ppm removal over pitch based ACFs by W/F of 2.5×10^{-3} g min ml^{-1} at 30°C. Without NO, SO_2 was removed completely for longer than 20h. While a concentration of NO of 500ppm reduced the stationary removal of SO_2 to 35%. More H_2O and a larger W/F increased SO_2 removal in the presence of NO. NO leaked freely without any removal except for the initial 1h while its outlet concentration increased very sharply from 0 to 100%. No reaction of NO was estimated at the stationary state while NO certainly inhibited the SO_2 removal by requiring larger H_2O concentration or W/F for the complete removal of SO_2.

TPDE spectrum of pitch based ACFs

Figure 5 shows the profiles of CO and CO_2 evolution from OG-20A, OG-15A, and OG-10A. CO_2 began to be evolved at about 180°C giving a highest evolution at 300°C, and then gradually decreased its amount to become null at 900°C regardless of the extent of activation of the fibers. CO began to be evolved at about 200°C and its amount increased gradually upto 500°C and then rapidly to 900°C where the maximum was observed. The amount of evolved CO increased with the increasing extent of activation and surface area. Significant retardation of NO without its stationary conversion should be studied in more details for scientific as well as technical view points.

DISCUSSION

The present study reported a remarkably high activity of a pitch based active carbon fiber of very large surface area after the heat-treatment at unusually high temperature of 1100°C. The activity observed in the present study allowed the complete removal of 1000ppm SO_2 at room temperature over OG-20A-H1100. A very small volume of reactor is designed by such a high activity. The active site for SO_2 removal is not identified. Large surface area and deoxygenated surface may provide more active sites of SO_2 oxidation and accelerate the elution of aq.H_2SO_4 with minimam H_2O from the active site because of high hydrophobicity.

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Table 1. Some Properties of Pitch Based Active Carbon Fibers.

ACFs	Ultimate analysis (wt%)					Surface area
	C	H	N	O	Ash	(m^2/g)
OG-5A	89.6	1.1	0.7	8.2	0.3	480
OG-15A	92.5	0.9	0.4	5.8	0.4	1550
OG-20A	93.9	0.9	0.3	4.6	0.5	1860
OG-20A-H900 [a)]	95.8	0.6	0.3	2.8	0.5	1690
OG-20A-H1100 [a)]	97.5	0.1	0.2	1.6	0.6	1570
OG-20A-H1200 [a)]	98.0	0	0.2	1.2	0.6	1420

a) Calcination temperature (℃)
OG-series : Pitch based active carbon fiber

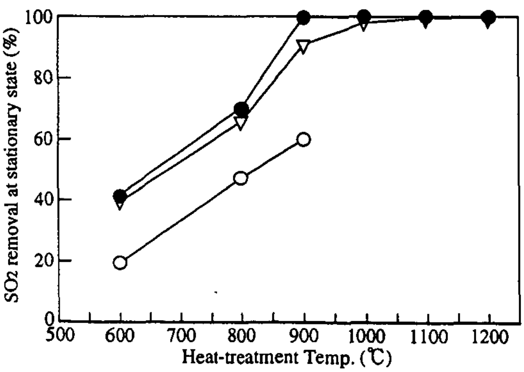

Figure 1 The effects of heat-treatment temperature for SO_2 removal over Pitch-ACFs
SO_2 1000ppm, O_2 5 vol%, H_2O 10 vol%
W/F = 2.5×10^{-3} g min mL^{-1}, Reaction Temp. 30℃
○: OG-5A (S.A. 480m^2/g)
▽: OG-15A (S.A. 1550m^2/g)
●: OG-20A (S.A. 1850m^2/g)

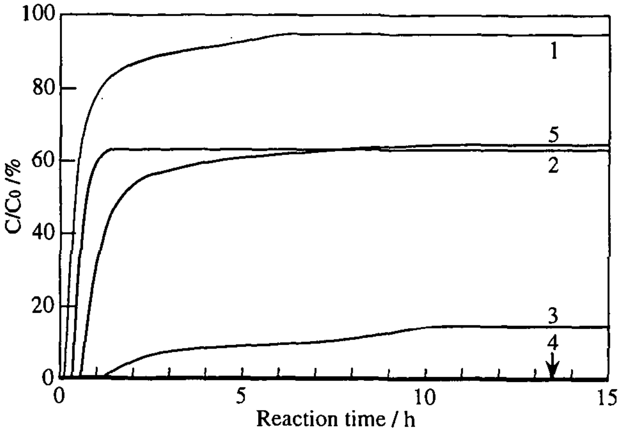

Figure 2 Breakthrough Profiles of SO_2 over Pitch-ACFs at 30℃
SO_2 1000ppm, O_2 5 vol%, H_2O 10 vol%
W/F : 1.0×10 g min mL
1: OG-20A
2: OG-20A-H900
3: OG-20A-H1000
4: OG-20A-H1100
5: OG-20A-H1200

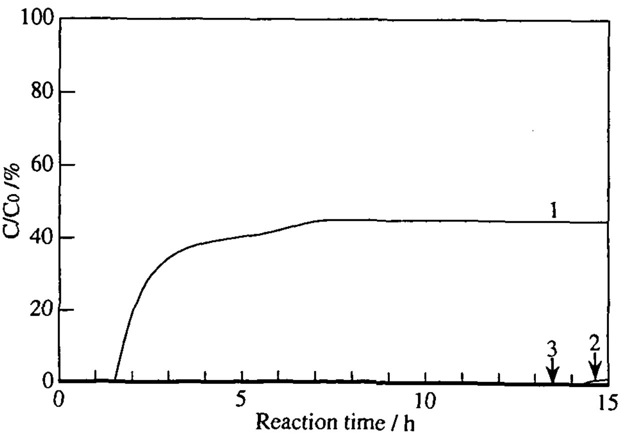

Figure 3. Breakthrough Profiles of SO_2 over Heat-treated Pitch-ACF at several H_2O concentration at 30℃
SO_2 1000ppm, O_2 5 vol%, H_2O 10 vol%
W/F : 1.0×10^{-3}g min mL^{-1}
ACF : OG-20A-H1100
H_2O 1 : 5vol%, 2 : 7.5vol%, 3 : 10vol%

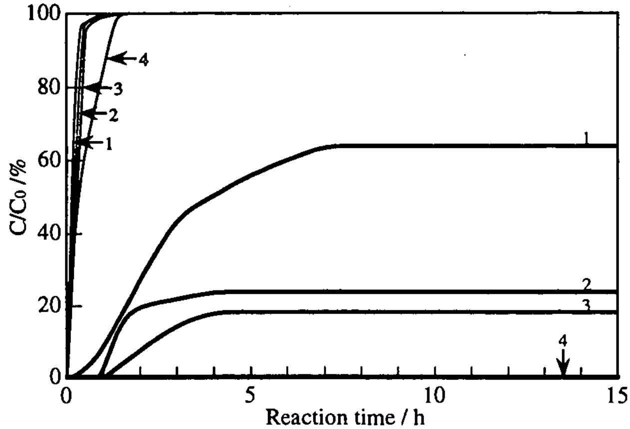

Figure 4 Breakthrough profiles of SO_2 and NO over OG-20-1100 at 30℃
SO_2 : 500 ppm, NO : 500 ppm, O_2 : 5 vol%, $W/F = 1.0 \times 10^{-3} g \cdot min \cdot ml^{-1}$
H_2O 1 : 10 vol%, 2 : 15 vol%, 3 : 20 vol%

4 : $W/F = 2.5 \times 10^{-3} g \cdot min \cdot ml^{-1}$; H_2O : 10%

SO_2 : ——
NO : ——

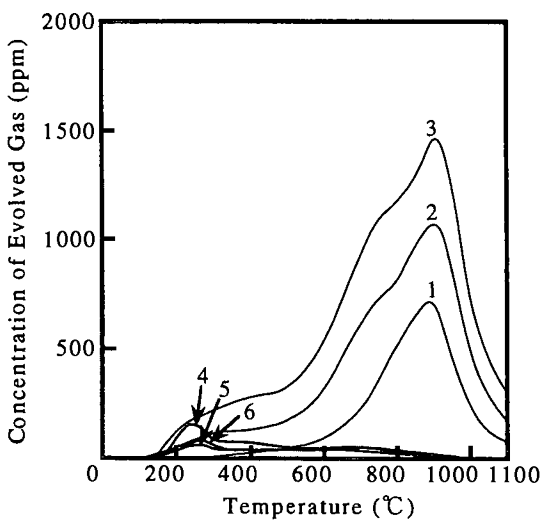

Figure 5 TPDE spectra of CO and CO_2 evolution from Pitch Based ACF
Weight : 100mg
Carrier gas : Helium
Flow rate : 100ml/min

Sample

CO	CO_2
1 : OG-5A	4 : OG-5A
2 : OG-15A	5 : OG-15A
3 : OG-20A	6 : OG-20A